Novel magnetic and electronic properties of kagomé-lattice cobalt-shandites(Abstract_要旨)

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論文題目	Novel magnetic and electronic properties of kagomé-lattice cobalt-shandites （カゴメ格子コバルトシャンダイトにおける新奇な磁性と伝導）		

（論文内容の要旨）

This thesis describes magnetic and transport properties of Co-based shandites $Co_3M_2S_2$ (M = Sn and/or In), which are candidates of quasi-two-dimensional (Q2D) strongly correlated electron systems, and consists of eight chapters. The interest is implied by its layered crystal structure that contains 2D-kagomé networks of magnetic Co atoms. The kagomé lattice, a corner-sharing triangular lattice, is a representative frustrated lattice where a thermodynamic stable state of the antiferromagnetic-coupled spin system is not trivially determined due to the geometric-origin competitions of spin-spin interactions. The Co-based shandites have been investigated mainly using polycrystalline samples and some interesting properties were found: the half-metallic ferromagnetic state in $Co_3Sn_2S_2$, the magnetic instability controlled by electron number in $Co_3Sn_{2-x}In_xS_2$, high thermoelectric properties of Co_3SnInS_2. However, investigations from the above-mentioned viewpoint, Q2D kagomé system, have not been carried out. For this purpose, investigations using single crystals are essential. This thesis reports successful growth of single crystals of two series-compounds of Co-based shandites, $Co_3Sn_{2-x}In_xS_2$ and $Co_{3-y}Fe_ySn_2S_2$ and novel and exotic properties, namely, (i) highly Q2D itinerant electron magnetism, (ii) emergence of a chiral spin state in the vicinity of the ferromagnetic-nonmagnetic quantum critical point (QCP), (iii) low-field anomalous phase very close to T_C, and (iv) emergence of exotic Q2D electronic state, which may be a Dirac semimetal state. Chapters 1 and 2 describe introduction and experimental procedures, respectively.

Chapter 3 describes single crystal growth of two series-compounds of Co-based shandites $Co_3Sn_{2-x}In_xS_2$ ($0 < x \leq 2$) and $Co_{3-y}Fe_ySn_2S_2$ ($y \leq 0.5$). The crystals were successfully grown by flux method and modified Bridgeman method. Using the flux method, sufficiently large hexagonal plate-shaped single crystals were obtained. $Co_3Sn_{2-x}In_xS_2$ single crystals were grown out of stoichiometric Sn and In self-flux, and/or Pb flux while $Co_{3-y}Fe_ySn_2S_2$ crystals were grown out of the Sn self-flux. Much larger single crystals of $Co_3Sn_{2-x}In_xS_2$ (~5 cm in length and 1 cm in diameter) were grown by using a modified Bridgeman method of slow cooling of vacuum-sealed polycrystalline powders in a vertical temperature-gradient furnace. The shandite structure with $R\bar{3}m$ symmetry was confirmed by powder x-ray diffraction and the crystal structure parameters were refined by the Rietveld analysis. Wavelength-dispersive x-ray spectroscopy indicated the successful growth of $Co_3Sn_{2-x}In_xS_2$ in the whole range of x and the growth of $Co_{3-y}Fe_ySn_2S_2$ up to $y = 0.5$.

Chapter 4 describes comprehensive magnetization measurements for the grown single crystals of Co-based shandites. In consistence with literature, $Co_3Sn_2S_2$ exhibits a ferromagnetic transition at Curie temperature T_C ~ 173 K with a strong uniaxial anisotropy. The ferromagnetic order is suppressed by In- and Fe-substitutions and the ferromagnetic-nonmagnetic quantum phase transition was found at around x_c (y_c) ~ 0.8. The obtained magnetic parameters of both systems; the Curie temperature T_C, effective moment p_{eff} and spontaneous moment p_s; exhibit almost identical variations against the In- and Fe-concentrations, indicating significance of the electron count on the magnetism in the Co-based shandite. Analyses of the magnetizations based on the extended Q2D spin fluctuation theory clearly reveals a highly Q2D itinerant electron character of the magnetism in $Co_3Sn_{2-x}In_xS_2$ and $Co_{3-y}Fe_ySn_2S_2$. It is a natural consequence of the layered crystal structure of the Co-based shandites.

Chapter 5 describes a chiral spin state observed in the vicinity of the quantum critical point (QCP) of $Co_3Sn_{2-x}In_xS_2$ through a combined work of the magnetization and magneto-transport measurements. A distinct positive topological Hall effect (THE) was observed at low temperature (T < ~ 7 K) and low field (H < ~ 0.2 T) regions, indicating an emergence of the non-trivial spin state with finite uniform chirality. This chiral spin state is interpreted as a consequence of the combination of the inherent Dzyaloshinskii-Moriya (DM) interaction in the kagomé Co-network built in the shandite structure, ferromagnetic order, and in-plane spin fluctuations enhanced near the QCP.

Chapter 6 reportes an anomalous phase (A-phase) in the vicinity of T_C and at very low fields (≲ 0.04 T), which was discovered within the ferromagnetic ordered phase of $Co_3Sn_{2-x}In_xS_2$. Precise magnetization and ac susceptibility measurements at very low magnetic fields (below the saturating field of ~ 1kOe) were performed and extremely slow dynamics, its characteristic relaxation time is longer than 10 sec, was found near the phase transition temperatures/fields between the anomalous phase and ferromagnetic/paramagnetic phases. These characteristic slow dynamics are very similar to those observed in the magnetic skyrmion materials such as (Fe,Co)Si and Cu_2OSeO_3, where the 2D triangular arrangement of large-scaled objects of topologically-protected vortex-like spin texture (magnetic skyrmion) is stabilized. With considering the possible DM interaction and similarity to the known magnetic skyrmion systems, the experimental results suggest the presence of a skyrmion-like topologically protected spin texture in the A-phase of $Co_3Sn_{2-x}In_xS_2$.

Chapter 7 descibes exotic electronic state in $Co_3Sn_{2-x}In_xS_2$ for x ~ 1.0, which were also discovered by resistivity and heat capacity measurements using single crystals. The Fermi level of $Co_3Sn_{2-x}In_xS_2$ is tuned by the In-substitution and it changes from the electron- to hole-band at around x ~ 1.0. An exotic semimetallic behavior, a logarithmic divergence of the resistivity against temperature, was observed in a very narrow x-region at x ~ 1.0, accompanying an anomalously enhanced anisotropy of the *ab*-plane and *c*-axis resistivity. Simultaneously, an absence of the T-linear term of the specific heat, and a strongly enhanced T^3-term instead, were found. All indicate an unconventional electronic state with anomalously small Fermi surface very close to x ~ 1.0. With considering the enhanced T^3-term of the specific heat, that is a T^3-term of electronic specific heat, a linear dispersive electron state and an emergent Dirac electron state in this layered kagomé system is suggested.

Chapter 8 is concluding remarks of the thesis.

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（論文審査の結果の要旨）

カゴメ格子は正三角形が頂点を共有する 2 次元格子であり、その格子点にスピンを配置したカゴメ磁性体では格子の幾何学に由来したスピン間相互作用のフラストレーションや反対称 Dzyalosinsky-Moriya(DM)相互作用などに起因する量子スピン液体や非自明な磁気構造などの新奇な物性が期待される。近年では、非自明な磁気構造によって誘起されるマルチフェロイック現象やトポロジカル伝導現象などが基礎科学の観点のみならずスピントロニクスなどの応用面からも注目されている。本論文は、遷移金属原子が組むカゴメ格子が層状に重なった結晶構造をもつシャンダイト化合物 $Co_3Sn_{2-x}In_xS_2$ の単結晶を育成し、その磁気的・電気的特性を調べたもので、カゴメ格子に起因した特異な物性を多数見出し、それをまとめている。得られた主な成果は以下の通りである。

１．$Co_3Sn_2S_2$ はキュリー温度 173 K の金属強磁性体であるが、In 置換により強磁性転移は抑制され、In 濃度 $x_c \approx 0.8$ で非磁性に量子相転移する。磁化過程をスピンゆらぎの理論で解析したところ、スピン相関が著しく異方的であることが分かった。

２．$Co_3Sn_{2-x}In_xS_2$ の強磁性状態の極低磁場領域で、キュリー温度近傍に低温の強磁性とも高温の常磁性とも異なる新たな磁気相が存在することを発見した。この磁気相は強磁性スピン配列のトポロジカル欠陥が配列したスカーミオン格子様状態と考えられる。

３．$Co_3Sn_{2-x}In_xS_2$ の磁気秩序状態は In 低濃度領域では非常に強い一軸性の磁気異方性をもつが、臨界濃度($x_c \approx 0.8$)に近い濃度ではそれが急激に弱まり Co スピンの面内成分が大きくなっている。詳細なホール抵抗測定により $x > 0.5$ の領域ではトポロジカルホール抵抗が観測され、伝導電子にベリー位相を与えるスピンカイラリティ秩序が出現していることが分かった。

４．$Co_3Sn_{2-x}In_xS_2$ では In 置換による電子数の減少により $x = 1$ 近傍でキャリアが電子からホールに変化するが、$x = 1$ 近傍で(i) 電気抵抗の異方性の特異的な増大、(ii) 電気抵抗の 0 K に向けての対数発散、(iii) 温度に線形な電子比熱の消失と 3 乗項の増大、が起こることを見出した。これら異常は、線形な分散関係をもつバンド交点が存在し、フェルミエネルギーが丁度その点に一致した、いわゆるディラック電子状態をとると考えることで説明可能である。

以上のように、本論文では、カゴメ格子化合物 Co シャンダイトで特異な物性を数多く見出し、学術上、実際上寄与するところが少なくない。また、上記２－４で見出された現象は応用上の観点からも興味深い結果である。よって、本論文は博士（工学）の学位論文として価値あるものと認める。また、平２８年１２月１９日、論文内容とそれに関連した事項について試問を行って、申請者が博士後期課程学位取得基準を満たしていることを確認し、合格と認めた。